

SOLUTIONS to H/w #6

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First we prove the following fact: for an ideal gas in some conservative force field the ~~the~~ average concentration is proportional to $e^{-U(\vec{r})/\tau}$, where τ is the temperature of the gas, $U(\vec{r})$ - the potential energy of one particle.

Proof. Consider one particle as our system. It's in thermal contact with the other particles, which we'll treat as the reservoir. Thus the probability for this particle to be in a certain quantum state s is

$$p_s = \frac{1}{Z} e^{-E_s/\tau}$$

E_s includes the potential energy term and the "intrinsic" energy term, i.e.

$$E_s = U(\vec{r}) + E'_s$$

This "intrinsic" energy includes the kinetic energy plus whatever internal energy the molecule might have. Now consider two states - identical in terms of the "intrinsic" variables (like momentum, internal configuration of the particle), but different in positions (say \vec{r}_1 and \vec{r}_2). The ratio of the probabilities is:

$$\begin{aligned} \frac{p_{s1}}{p_{s2}} &= \frac{e^{-E_{s1}/\tau}}{e^{-E_{s2}/\tau}} = \frac{e^{-U(\vec{r}_1)/\tau} - E'_{s1}/\tau}{e^{-U(\vec{r}_2)/\tau} - E'_{s2}/\tau} = \{ \text{since } E'_{s1} = E'_{s2} \} \\ &= \frac{e^{-U(\vec{r}_1)/\tau}}{e^{-U(\vec{r}_2)/\tau}} \end{aligned}$$

That shows that $p_s = A_{s1} e^{-U(\vec{r})/\tau}$, where A_{s1} depends on the "intrinsic" variables (label them collectively as s') but not on the location \vec{r} . Now, the probability to be at location \vec{r} is the sum over all the states with location \vec{r} , i.e.

$$p(\vec{r}) = \sum_{\substack{\text{all intrinsic} \\ \text{states } s'}} A_{s'} e^{-U(\vec{r})/\tau} = e^{-U(\vec{r})/\tau} \sum_{s'} A_{s'} = B e^{-U(\vec{r})/\tau}$$